SCIENCE FOR CERAMIC PRODUCTION

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STRUCTURE AND PROPERTIES OF CERAMIC MATERIALS AFTER LASER TREATMENT

A. S. Krasnikov,[1] A. I. Berezhnoi,[1] and L. I. Mirkin[1]

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The effect of laser radiation with varying pulse duration and pumping voltage on ceramic materials is investigated. The amorphization of the ceramic structure in the laser beam action zone is established. The treatment of materials by a laser beam results in emergence of radial microcracks 40 – 50 μm long.

Laser beams have gained wide acceptance in ceramic production technologies [1]. Various types of ceramics are used as materials for production of computer elements and substrates for hybrid integrated circuits, and laser treatment has a prominent place in their production technologies.

The increased degree of miniaturization and integration of electronic requires special processing technologies which ensure the absence of mechanical contact between the machining tool and the ceramic workpiece and a high degree of treatment localization. This makes laser treatment the only contact-free technique for formation of holes, cavities, and other elements in ceramics.

In order to elucidate the expediency of using the laser beam in solving a specific technological problem, it is necessary to understand the mechanism of the laser radiation effect on material and the feasibility of using the existing lasers, which is determined both by the radiation parameters (wavelength, radiation energy and power, pulse duration, the beam diameter variation range) and by material characteristics (reflecting capacity and absorption coefficient on the laser radiation wavelength, heat conduction, thermal conductivity). The main parameters of laser radiation which determine the radiation absorption by the material, as well as heating, melting, and evaporation processes, are the radiation wavelength and the pulse energy (or power) [2].

In order to use a laser in various technological operations on ceramics, such as scribing (marking) and hole broaching, it is necessary to know the effect of the laser radiation parameters on the material.

[1] Ryazan' State Pedagogical University, Ryazan', Russia; Moscow Open University, Moscow, Russia; Institute of Mechanics at Moscow State University, Moscow, Russia.

According to the data in [3], such companies as Laser Tech Services (Denmark), which is one of the world leaders in laser treatment of ceramics for microelectronics, require lasers which are able to penetrate to a specific depth from the material surface and produce a specific hole profile at frequencies over 10^3 Hz (pulse/sec) and linear motion speed > 10 m/min without microcracking.

It was suggested in [1] that when holes are made in corundum ceramics using laser radiation, the crystal phase is melted, and the melt migrates towards the heated walls of the emerging hole and is later carried to the surface with emergence of a typical amorphous ridge. This hypothesis had to be experimentally proved or disproved.

The main method used by the authors to solve this problem was the small diaphragm method [4, 5]. Additional data on the structural state of the sample can be obtained by analyzing the variations in its structure-sensitive properties. The latter include mechanical properties and, primarily, microhardness [6]. This property was used by us to obtain additional information on the sample structure in the zone of the laser beam action.

The analyzed samples of VK-100-1 ceramics (1 – 7) had the same chemical composition (wt.%): 99.8 Al_2O_3 and 0.2 MgO; but were treated by different lasers. The laser radiation parameters in interaction with polycrystalline ceramics VK-100-1 and VK-94-1 are shown in Table 1.

The x-ray analysis of the polycrystalline ceramics demonstrated that the crystalline phase of α-corundum (α-Al_2O_3) was present in all radiated and non-radiated samples.

The microstructure of non-radiated VK-100-1 ceramic samples (Fig. 1*a*) is characterized by a dense coarse-crystalline structure with 30 – 40 μm corundum grains (the light-

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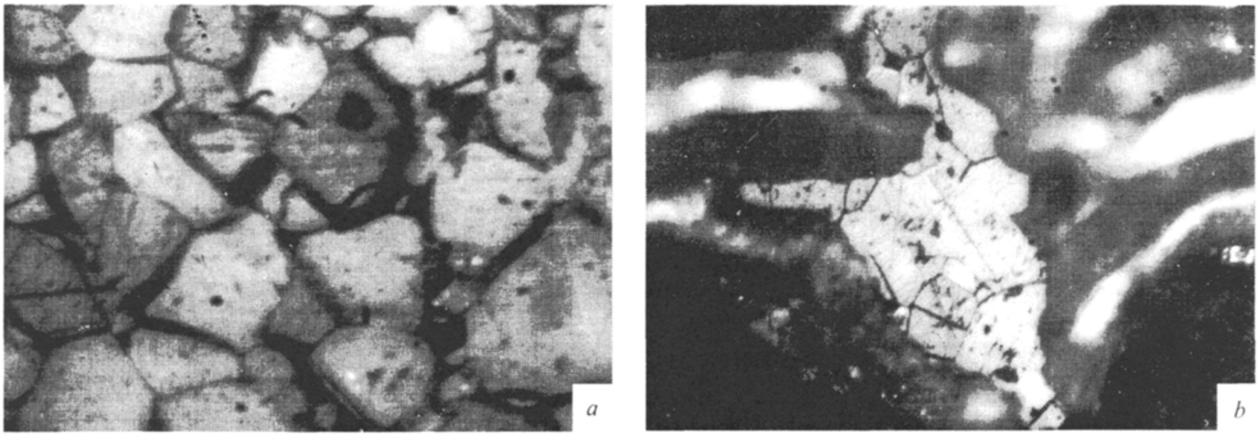

Fig. 1. Microstructure of VK-100-1 ceramic samples before (*a*) and after (*b*) laser radiation. The site between 4 holes (×440).

colored sites). The photo exhibits clearly defined grain boundaries, as well as dark sites which are pores and pickling holes left by grain dislocations. The presence of small pores located inside individual grains is possible as well. At the same time, the microstructure of the ceramic samples radiated by millisecond pulses exhibits destroyed segments of the crystalline structure and fused material sites which are amorphous formations (Fig. 1*b*). The laser treatment of ceramics using a pulse duration of 70 nsec results in the emergence of even boundaries without the amorphous interlayer and typical ridges.

The obtained data agree well with the results in [7, 8]. The thickness of the melted material layer can be evaluated according to the formula [7, 8]

$$d = \frac{\tau\alpha}{r} \ln \frac{t_v}{t_m},$$

where τ is the laser pulse duration; α is the thermal conductivity of the material; r is the radius of the laser beam action zone; t_v and t_m is the vaporization temperature and the melting point of the material.

Taking $t_v = 3050$°C and $t_m = 2800$°C, $d = 0.026$ cm/sec and $r = 68.2$ μm for aluminooxide ceramics, at $\tau = 0.400$ msec we obtain $d \sim 5.5$ μm, which agrees with the results of the measurements performed on the microstructural photos. The coarse-grained ceramic structure in the zone of laser radiation action is crushed and pulverized. Since usually $r \sim 0.01$ cm, the ceramics manifest clearly visible inhomogeneity of the structure, composition, and properties of the thermal effect zone along with the small size of this zone. This inhomogeneity is related to the high heating and chilling rates and to the substantial temperature gradients and pulse pressures.

The amorphous phase of some samples reveals microcracks whose length reaches 20 – 40 μm and even more. These microcracks are especially perceptible in VK-94-1 ceramics (sample 5). The microcracks originate at the boundary between the amorphous and the crystal phases and exit radially to the hole edge. The size of the microcracks reaches 50 – 100 μm.

The emergence of microcracks, in our opinion, is determined by the stressed state which originates in the material due to the sharp difference in the CTLEs of the amorphous and the crystal phases of ceramics. The microcracks can emerge both on the surface and inside the ceramics. In the

TABLE 1

Sample	Laser type	Laser working material	Pulse duration, msec	Pulse power, J	Diameter, mm	
					of the hole	of the spot
1	4222-F2	Glass with neodymium	0.3	2.0	1.0	0.2
2	The same	The same	0.3	2.0	0.2	0.2
3	The same	The same	0.3	2.0	6.0	0.2
4	The same	The same	0.3	2.0	3.0	0.2
5	Kristall-6	The same	0.6	5.4	0.3	–
6	Kvant-12	Aluminum-yttrium garnet	1.5	3.0	0.3	–
7	Kvant-16	The same	0.6	7.0	0.5	–

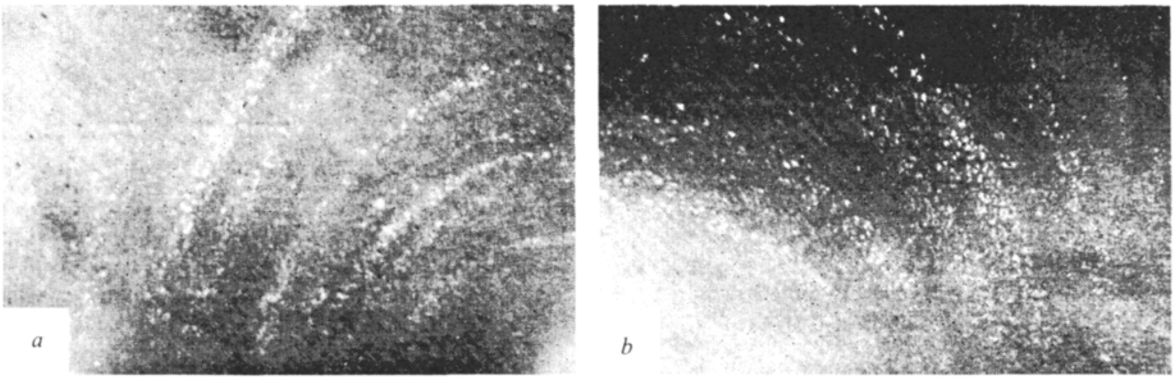

Fig. 2. X-ray patterns of VK-100-1 ceramics before (*a*) and after (*b*) the effect of laser radiation.

latter case, this is apparently a consequence of thermal stresses arising in ceramics in the laser beam action zone under fast chilling or heating. A mechanism for crack origination in ceramics may be the accumulation of dislocations in front of obstacles impeding dislocation migration (at the site of slide planes intersection, at the grain boundaries, and near the surface). The accumulation of dislocations produces local stresses which are sufficient for merging of several dislocations and formation of a crack nucleus.

The structure of VK-100-1 ceramics is characterized by sufficiently large grain sizes, which is well supported by the x-ray structural analysis data. In fact, the x-ray interference lines are divided into point reflections (Fig. 2*a*). The x-ray pattern of the same sample after laser treatment (Fig. 2*b*) exhibits an increase in scattering intensity at low angles, which is evidence of the increased content of the amorphous phase. The measurement results of the microhardness of a series of ceramic samples are shown in Table 2.

As can be seen, the initial ceramic samples have a high level of microhardness (13.5 GPa), while the microhardness in the beam action area is equal to 2.5 – 9.7 GPa. The variation of microhardness correlates with the change in the pulse duration, the radiation conditions being equal. In this context, the investigated samples should be divided into two groups: the samples (3, 4, 8) treated by free generation radiation and the sample (1) radiated in the switched quality-factor regime.

Of special interest is the radiation regime of sample 4 which exhibited the lowest value of microhardness equal to 2.5 GPa. This significant difference in microhardness of the initial ceramics and the ceramics subjected to laser radiation can only be accounted for by the amorphization of the sample structure in the beam action zone. These assumptions well agree with the results of the microstructural analysis using the metallographic method. The photos of sample 4 microstructure revealed the drop-shaped and elongated nuclei of the amorphous phase. It can be seen in Fig. 3 that the crack is filled with the amorphous phase. The x-ray structural analysis data also support the above assumptions (Fig. 4).

It is necessary to discuss the results of microhardness measurement of sample 1 treated by a LTI-502 laser in the switched Q-factor regime. The sample surface after laser treatment represents a grid of mutually perpendicular intersecting laser marks, i.e., scribing lines 150 μm deep deposited at a distance of 300 μm. These marks are stress concentrators, due to which the microhardness of the unfractured sample at the edges of the marks is one-fourth of the initial sample microhardness. The decrease in microhardness shown by the rest of the samples is determined by their stressed state, which is especially typical of sample 7.

TABLE 2

Sample	Laser type	Laser working material	Pulse duration, msec	Pulse energy, J	Average power, W	Pulse frequency, Hz	Microhardness, GPa		Microhardness ratio of radiated and non-radiated samples
							before radiation	after radiation	
1	LTI-502	–	100×10^{-9}	0.004	16	4×10^3	13.5	3.2	4.2
3	4222-F2	Glass with neodymium	0.3×10^{-3}	3	–	1.5	12.6	9.7	1.3
4	Kvant-1	Aluminum-yttrium garnet	1.5×10^{-3}	3	–	5	13.5	2.5	5.3
8	4222-F2	The same	2.5×10^{-4}	2	–	1.5	12.2	8.9	1.4

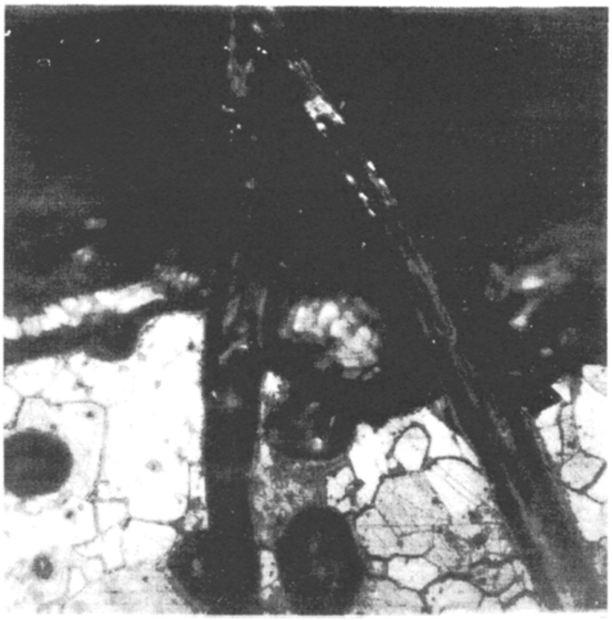

Fig. 3. Microstructure of VK-100-1 ceramic sample after treatment with laser beam for 1.5 msec.

In the case of broaching holes on a Kvant-12 unit by a laser beam with power flow of ~ 106 W/cm^2 and pulse duration exceeding 1 msec, the probability of emergence of radial cracks in ceramic material increases [7, 8]. With the minimum pulse duration (1.5 msec), the cracks start forming around single holes 90 – 120 μm in diameter when the pumping voltage reaches ≥ 50 V, and in a system of holes with an inter-center distance of 2 mm, the cracks start at ≤ 440 V. The emergence of cracks in this case can be prevented only by decreasing the pumping voltage to 380 V.

In this context, it is necessary to clarify the effect of different levels of pump voltage on the processes occurring in the laser action zone. Since the amorphous state of corundum is quite natural under certain conditions [9 – 11], the study of the phase composition of aluminum oxide ceramics in the laser beam action zone, as well as the chemical composition of the initial sample matrix and the zone of laser radiation action, is of particular interest. It is known that the chemical resistance of ceramics depends not only on its chemical composition, but also on its microstructure and phase composition. The presence of the vitreous phase has a great effect on chemical resistance. Thus, the presence of this phase substantially decreases the chemical resistance of corundum ceramics to acids and alkalis [12]. Since variations in the phase composition in the laser beam action zone can be expected, this should modify the chemical resistance of the material.

The considered VK-100-1 ceramic samples were shaped as flat plates with holes which were broached using different pump voltage levels ranging from 550 to 850 V with pulse duration of 2 msec [13]. The emergence of the typical amorphous ridge and radial microcracks reaching the hole edge and of microcracks filled with amorphous phase was observed at all levels of pump voltage. Amorphous formations of random shapes were visible on the hole walls. The microphotos exhibited hexagonal crystals of α-corundum of regular geometric shape. The metallographic analysis results agree well with the x-ray structural analysis data.

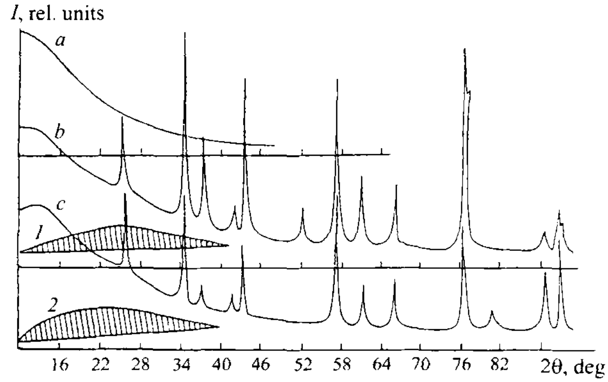

Fig. 4. X-ray diffraction patterns obtained on ceramic sample 4: *a*) x-ray scattering in air without the sample; *b*, *c*) x-ray scattering obtained for the initial sample with the isolated amorphous halo (*1*) and the radiated sample with the isolated amorphous halo (*2*), respectively.

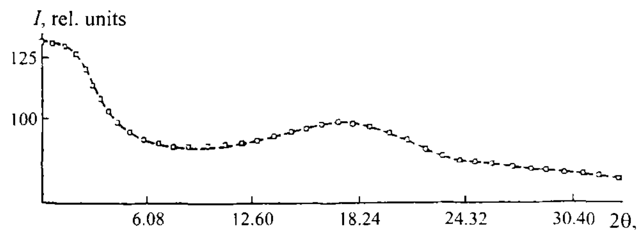

Fig. 5. Photometric curve of radiation intensity distribution as a function of the scattering angle.

The experimental data obtained by probing one of the holes indicate the amorphization of the structure in the laser beam action area, which is manifested in the formation of a symmetric amorphous halo in the x-ray pattern.

The photometry of the amorphous halo sites is of special interest. For this purpose, the intensity distribution was determined as a function of the scattering angle in the x-ray pattern using a MF-2 microphotometer. The distribution curves constructed for the VK-100-1 ceramic samples indicate that the distribution of x-ray scattering intensity has the characteristic maximum for an angle $2\theta = 16°$ corresponding to the near order. It corroborates the transition from the crystalline state to the amorphous state in the laser beam action area (Fig. 5). The obtained results are supported by the data of the electron microscope study of the area. The microphotos reveal the formation of typical amorphous ridges, which attests to the carryover of melted material to the surface of the hole inlet channel.

Samples of VK-100-1 ceramics and sapphire were subjected to chemical pickling, and their structure and micro-

TABLE 3

Pumping voltage, V	Vickers microhardness of ceramics, GPa		
	initial	after laser radiation	after pickling of the laser action zone
750	20.6	18.7	21.3
550	20.0	17.0	19.9
550	20.0	16.1	19.9
550	28.5	20.6	24.4
750	22.0	–	16.6
750	21.0	18.7	28.3
800	19.0	18.8	28.3
750	19.6	13.9	24.4
850	22.0	16.5	36.2
650	48.8	15.6	33.3
650	28.5	15.9	28.3
650	21.3	17.7	19.9

hardness were studied before and after pickling. If the amorphous phase dissolves in the beam action zone, one can expect variations in the mechanical properties of the ceramics, in particular, variations in microhardness. The metallographic analysis of VK-100-1 ceramic samples before and after pickling reveals partial dissolution of the amorphous phase after acid pickling. The holes broached by the laser beam acquire a more regular geometric shape and their visible diameter changes slightly, which is probably related to the removal of the vitreous phase present in the hole inlet channel. The amorphous filaments and ledges which are present on the hole channel walls disappear after pickling. In double holes, the thickness of the jumper decreases. After the sapphire sample is pickled, the hole channel acquires regular shape.

The correctness of the derived conclusions is well corroborated by the measurement results of the sample microhardness in the laser beam action zone (Table 3). As can be seen, the microhardness of most samples substantially increases after pickling. This can be explained by the decrease in the amorphous phase content in the beam action area.

The study of the chemical composition indicated that the laser beam action zone is richer in aluminum, as compared to the initial sample matrix. The reason probably consists in the fact that all low-melting additives in ceramics evaporate under the laser radiation effect, and the laser action area after the formation of amorphous phase is enriched with aluminum. At the same time, all initial chemical elements are preserved in the sample. The amount of silicon registered in the sample matrix is insignificant. It should be noted that x-ray phase analysis revealed the existence of a small amount of the amorphous phase in the initial sample matrix.

Thus, laser radiation of ceramics leads to amorphization of the corundum phase in the beam action zone, and this process is most intense in the upper portion of the hole channel. The degree of amorphization depends on the duration of the laser radiation pulse.

Laser treatment decreases microhardness in the beam action zone and results in the formation of radial cracks up to 40 – 50 μm long.

The microhardness of samples in the zone of the laser beam action before pickling is lower than that after pickling, which can be accounted for by the increased content of amorphous phase in the zone.

The precision of the holes made in ceramics by laser radiation largely depends on the phase composition. An increase in the vitreous phase content decreases the precision of the hole treatment.

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